Hydrogenation of Butynediol to Cis-Butenediol Catalyzed by Pd-Zn-$CaCO_3$: Reaction Kinetics and Modeling of a Batch Slurry Reactor

An experimental study of the kinetics of hydrogenation of butynediol has been reported using Pd-Zn-$CaCO_3$ catalyst in a slurry reactor. The effects of catalyst loading, butynediol concentration, H_2 partial pressure, butenediol (product concentration, temperature, and agitation speed on the rate of hydrogenation have been studied using a stirred pressure reactor. The initial rate data showed that the rate is proportional to the square root of H_2 pressure, while increase in butynediol concentration inhibited the reaction. A Langmuir–Hinshelwood-type rate model has been proposed based on these data and the kinetic parameters evaluated. The values of the activation energy E and the heat of adsorption of butynediol $(-\Delta H)$ evaluated were 38.30 kJ/mol and −9.87 kJ/mol, respectively.

Batch reactor models were derived based on the rate expression obtained from the initial rate data for variable pressure as well as constant pressure conditions. The predictions of the model were compared with experimental data obtained over a wide range of conditions. The results agreed well within 5–7% error. Use of the pressure vs. time data for evaluation of kinetic and mass transfer parameters is also demonstrated.

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SCOPE

Hydrogenation of butynediol is an industrially important reaction in the manufacture of cis-butenediol, which is a raw material for Endosulfan (insecticide) and vitamin B_6. Generally, this reaction is carried out using supported Fe, Ni, or Pd catalysts in a slurry or a trickle-bed reactor. In order to selectively produce cis-butenediol, a modified catalyst has to be used such as Lindlar's catalyst (Pd-$CaCO_3$ poisoned with lead or zinc acetate). The purpose of the present work was to investigate the reaction kinetics of hydrogenation of butynediol to butenediol using Pd-Zn-$CaCO_3$ catalyst and application to modeling of a batch slurry reactor. Based on this catalyst, a process for butenediol has been developed in our laboratory. A process based on supported Fe catalyst is also described in the BIOS report of Appleyard and Gartshore (1946). The literature information on the reaction (Hoffman et al., 1976, Lindlar and Dubuis, 1966; Wood and Ritz, 1976a,b; and Fakuda and Tokishige, 1958) is mostly patented, and practically no attempts to investigate the reaction kinetics have been made so far.

In this work, the kinetic data were obtained using Pd-Zn-$CaCO_3$ catalyst in a stirred slurry reactor operated under isothermal conditions. The effect of various parameters such as catalyst loading, agitation speed, butynediol concentration, partial pressure of H_2, butenediol concentration, and temperature has been investigated. The pressure vs. time data were obtained over a wide range of conditions and the kinetic analysis was carried out from the initial rates and the integral batch reactor data.

Hydrogenation of butynediol is also an interesting three-phase catalytic system and provides a good example to study the modeling and scale-up of a three-phase slurry reactor. Very few attempts to model the slurry reactors based on intrinsic kinetics have been made so far. Therefore, experimental data were obtained in integral reactors at two scales (6×10^{-4} and 2×10^{-3} m^3 capacity). The predictions of the batch reactor models have been compared with experiments, and the applicability of the kinetic model over a wide range of conditions has been demonstrated.

CONCLUSIONS AND SIGNIFICANCE

Hydrogenation of butynediol to cis-butenediol occurs in the presence of Pd-Zn-$CaCO_3$ catalyst in a slurry rector. The kinetics of hydrogenation reaction was studied in a temperature range of 303–343 K using a stirred high-pressure slurry reactor. From the initial rate data, a Langmuir–Hinshelwood-type rate model was found to be satisfactory. The rate was found to be propor-

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tional to the square root of H_2 pressure, while an increase in butynediol concentration decreased the rate of reaction, indicating substrate inhibition. The data at 303-323 K were found to be in the kinetically controlled regime, while at 343 K gas-liquid mass transfer was found to be important. The rate equation represented the data at all temperatures satisfactorily. The values of activation energy E and the heat of adsorption of butynediol ($-\Delta H$) evaluated were 38.33 kJ/mol and −9.87 kJ/mol respectively.

In order to verify the applicability of the kinetic model under integral reactor conditions, theoretical models were developed for a batch slurry reactor for both constant and variable pressure conditions. Extensive experimental data were obtained in a batch reactor and compared with the predictions of the theoretical model. The agreement was found to be within 5-7% error. This indicates that the kinetic model represents the data over a wide range of conditions and can be used for design and scale-up purpose. It is demonstrated that pressure vs. time data can also be used to evaluate kinetic and mass transfer parameters. From the data at 343 K, k_La_B values were evaluated.

INTRODUCTION

Hydrogenation of butynediol selectively to cis-butenediol has become important due to the application of butenediol as a versatile chemical intermediate (e.g., in the manufacture of Endosulfan—an insecticide—and vitamin B_6). Lindlar-type catalysts (Lindlar and Dubuis, 1966) consisting of supported Pd doped with Zn acetate are known to give a selectivity for butenediol as high as 99.8%. The stoichiometric reaction is:

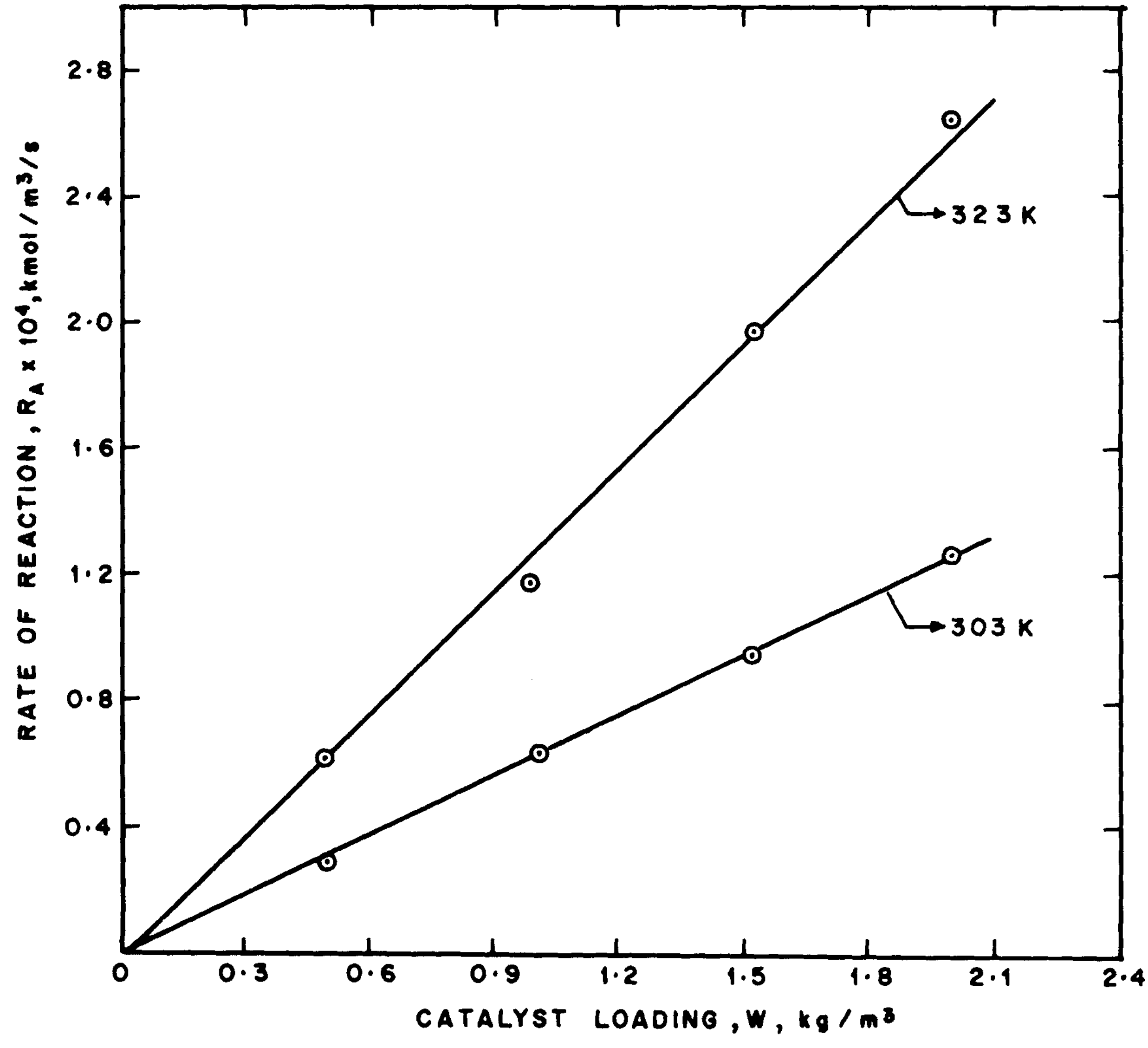

Figure 1. Effect of catalyst loading, *w*, on hydrogenation rate.

Initial butynediol concentration, B_{1i}, 2.32 kmol/m^2
Partial pressure of H_2, P_{gA}, 2.067 × 10^6 N/m^2
Stirrer speed, 13.3 Hz

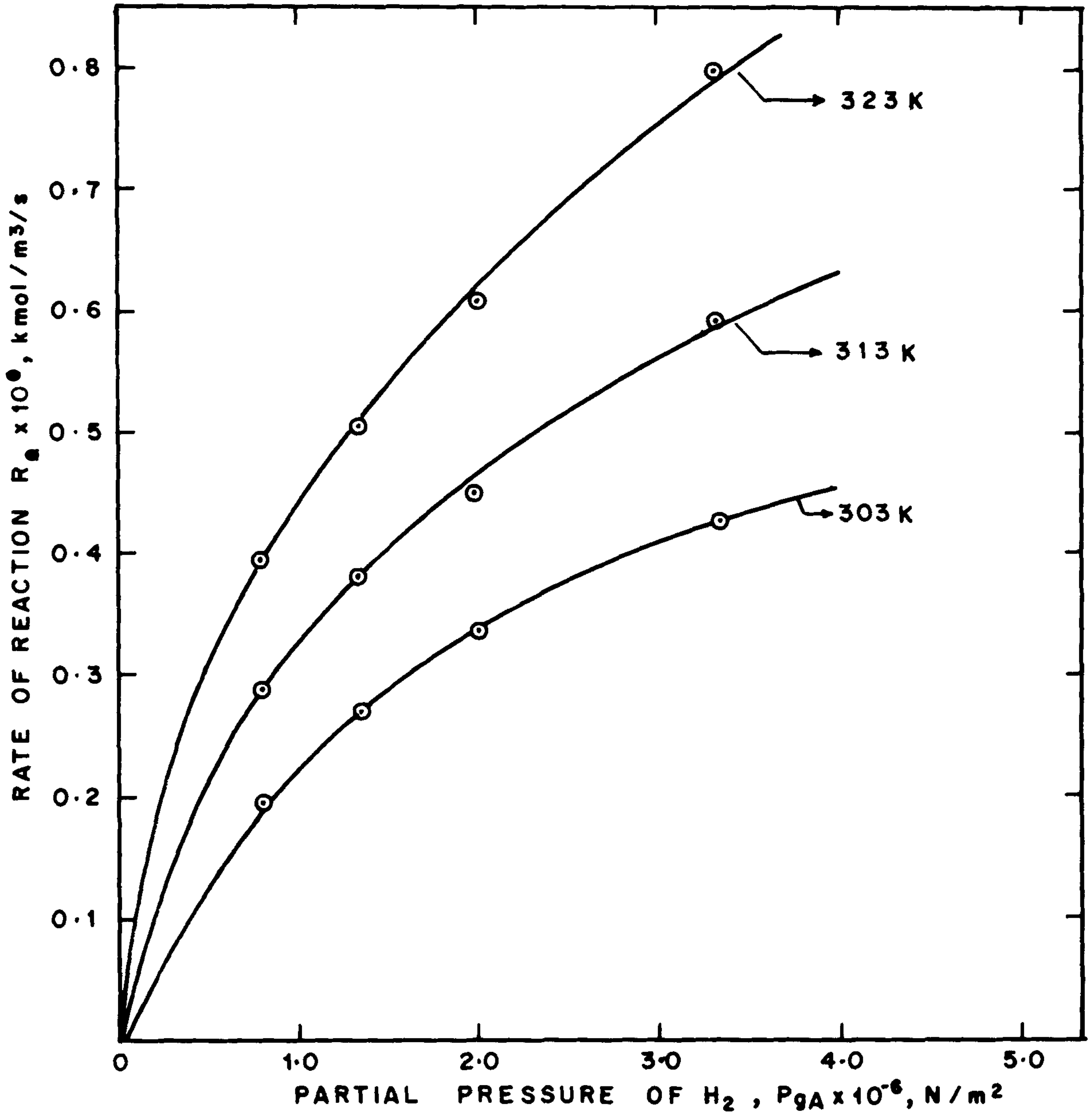

Figure 2. Effect of pressure on initial rate of hydrogenation.

Catalyst loading, w, 0.55 kg/m^3
Initial butynediol concentration, B_{li}, 2.32 kmol/m^3
Stirrer speed, 15 Hz

$$HOH_2C{-}C{\equiv}C{-}CH_2OH + H_2 \xrightarrow{Pd{-}Zn{-}CaCO_3} HOH_2C{-}CH{=}CH{-}CH_2OH$$

This is a three-phase reaction and is generally carried out in a slurry or trickle-bed reactor. For design purposes, there is a need to study the intrinsic kinetics of the above reaction using commercial catalyst and in the range of conditions used in practice. The objective of the present work was therefore to study intrinsic kinetics of selective hydrogenation of butynediol to butenediol using Pd-Zn-$CaCO_3$ catalyst. No attempts to investigate the kinetics of this reaction have been made so far. Further, it was also the goal of this research to develop batch reactor models incorporating the effect of external mass transfer and kinetics, and to study the scale-up of butenediol reactor based on the knowledge of the kinetics.

Thus, the experimental work was carried out in batch high-pressure stirred reactors of 6×10^{-4} and 2×10^{-3} m^3 capacities. In this work, H_2 pressure and liquid phase concentration vs. time data were analyzed using the batch reactor models and a Langmuir–Hinshelwood-type rate equation has been proposed. Application of the kinetic model for scale up of a batch slurry reactor is demonstrated.

EXPERIMENTAL

Catalyst Preparation and Materials

The catalyst used, Pd-Zn-$CaCO_3$, was a commercial catalyst developed in our laboratory for butenediol process. The preparation method was

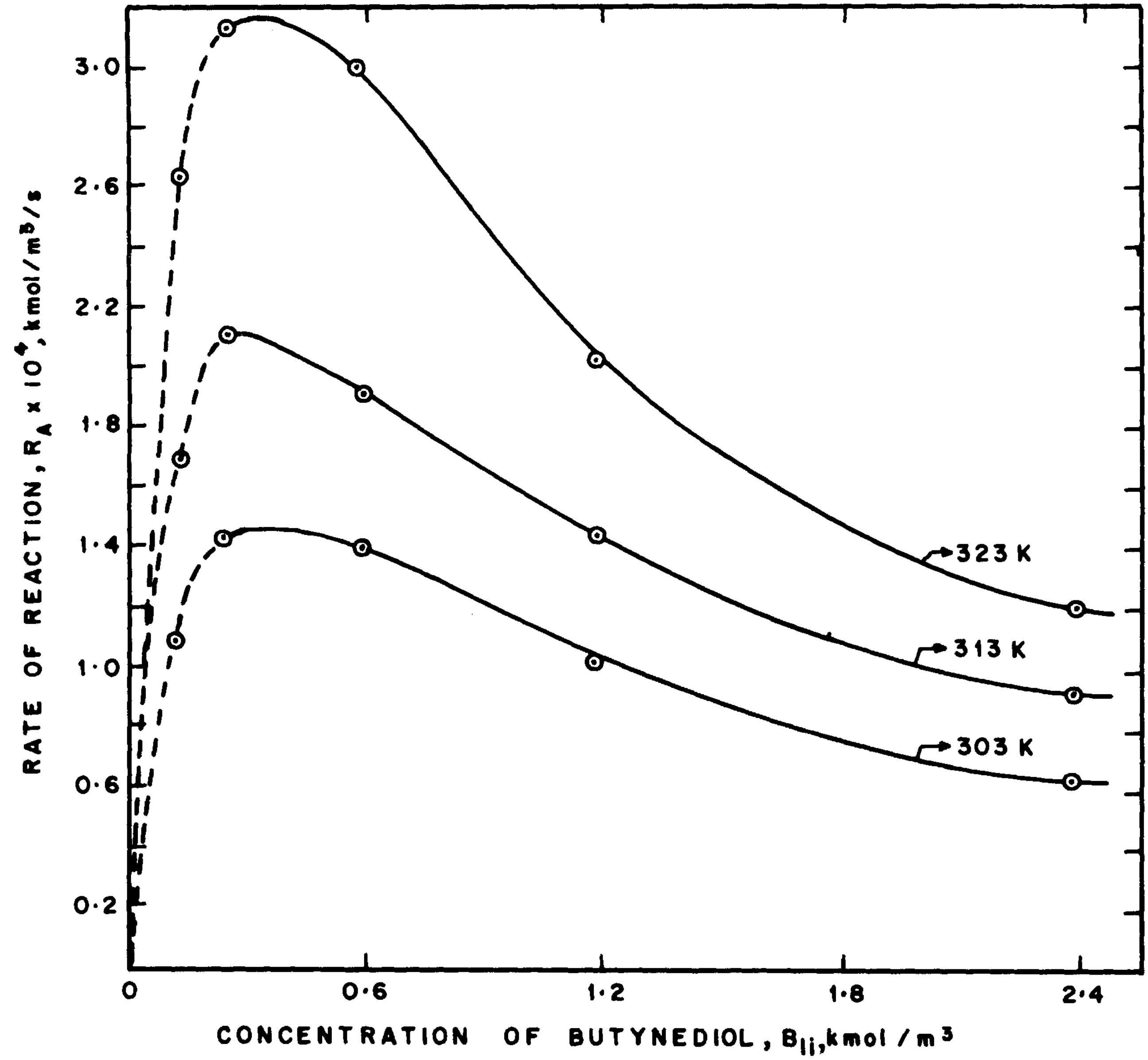

Figure 3. Effect of butynediol concentration, B_{li}, on initial rates of reaction.

Catalyst loading, w, 1.10 kg/m^3
Partial pressure of H_2, P_{gA}, 2.067 × 10^6 N/m^2
Stirrer speed, 15 Hz

similar to that described by Lindlar and Dubuis 1966). In a typical preparation 1.5×10^{-3} kg $PdCl_2$ was dissolved in aqueous hydrochloric acid solution. To this, 1.8×10^{-2} kg of precipitated $CaCO_3$ was added and the suspension was stirred for one hour at 358 K. Then 5% sodium formate solution was added and the mixture stirred for 1 h at 358 K. The catalyst was then filtered and washed with water. The moist catalyst paste was treated with 20% zinc acetate solution under reflux conditions for 30 min. The final catalyst was then filtered and dried in the oven. The physical properties of the catalyst are:

Average particle size, 4×10^{-2} m
Particle density, 2.17×10^{3} kg/m^3
Pore volume, 2.67×10^{-4} m^3/kg
Porosity, 0.58
Surface area, 1.2×10^{4} m^2/kg
Pd content, 1.0% (w/w)
Zn content, 12.2% (w/w).

Butynediol obtained as an aqueous solution (35%) was supplied by M/s. HOC Ltd. Hydrogen gas was obtained from M/s. Indian Oxygen Ltd. and was purified to remove traces of moisture and oxygen before use.

Apparatus and Procedure

Most experiments for intrinsic kinetic study were carried out in a batch pressure stirred autoclave (Parr Instruments) with 6×10^{-4} m^3 total capacity. This equipment was provided with automatic temperature control, variable stirrer speeds, and a pressure transducer with digital readout. Provision for sampling of the liquid was also made.

A solution of 2-butyne-1,4-diol of a desired concentration was prepared from 35% stock solution and was charged into the reactor along with a known quantity of the catalyst. The reactor was then flushed with nitrogen and a desired temperature was set. After this, the contents were flushed with H_2 twice, pressurized to the required level, and then the reaction was started by switching the stirrer on. The progress of the reaction was followed by observing the change in H_2 pressure at different times. In each run,

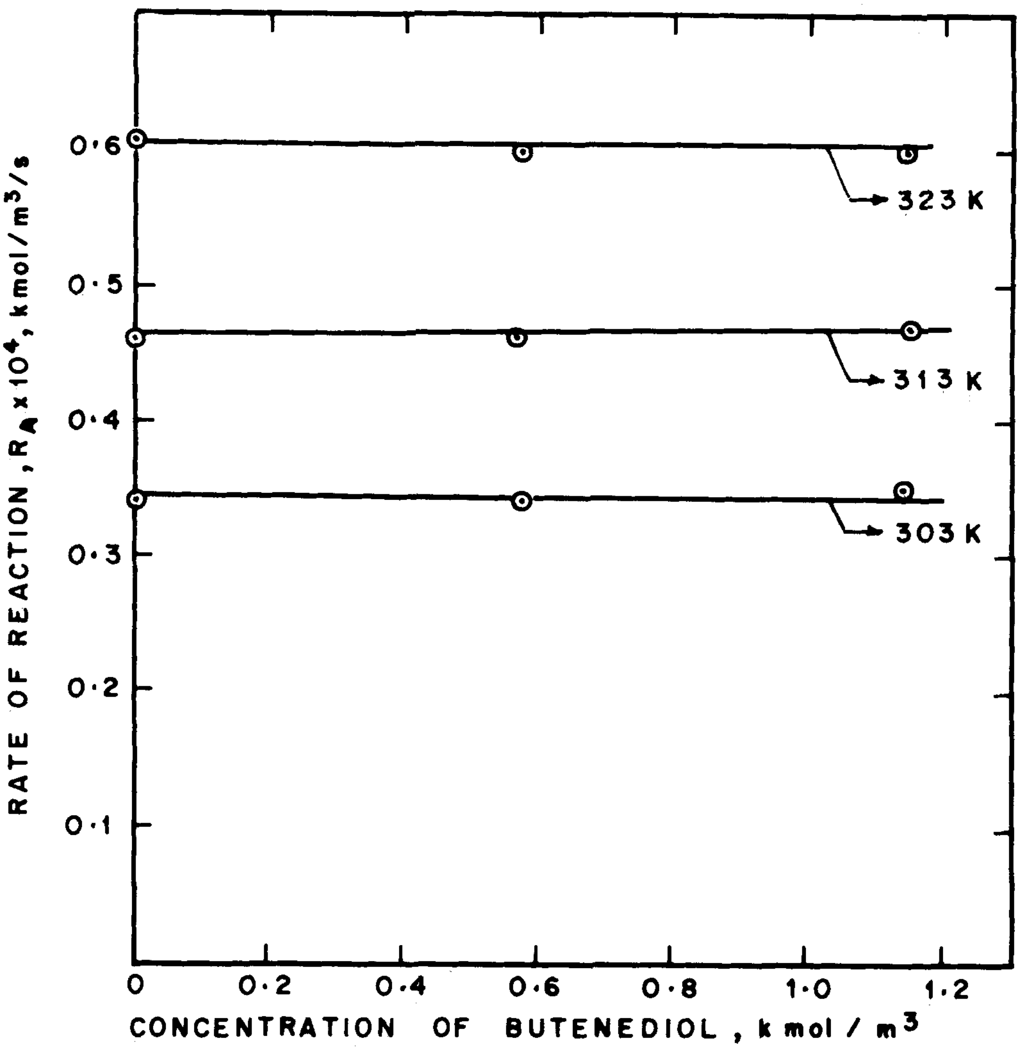

Figure 4. Effect of butenediol concentration, E_1, on hydrogenation

Catalyst loading, w, 0.55 kg/m^3
Butynediol concentration, B_{1i}, 2.32 kmol/m^3
Stirrer speed, 16 Hz

reactant and product concentrations were analyzed in initial and final samples. Some experiments were carried out at constant H_2 pressure using a special regulator between the autoclave and H_2 source. In these experiments, liquid samples were withdrawn at different times and analyzed for butynediol and butenediol. The analysis was carried out by gas chromatography. A Hewlet-Packard 5840 gas chromatograph equipped with FID, an electronic integrator, and automatic injection facilities was used. The stainless steel column used was 2.4 m long and packed with Carbowax 20 M (5%) on chromosorb W at a temperature of 473 K. A carrier gas flow rate of 6×10^{-5} m^3/s and injection temperature of 523 K were used.

Using the procedure described above, experiments at different operating conditions were carried out. The range of variables covered was:

Catalyst loading: 0.55–2.0, kg/m^3
H_2 pressure: 8.26×10^5–3.45×10^6 N/m^2
Agitation speed: 6.66–16.66 Hz
Concentration of butynediol: 0.116–2.32 kmol/m^3
Concentration of butenediol: 0–1.136, kmol/m^3
Temperature 303–343, K.

RESULTS AND DISCUSSION

The prime objective of the present work was to investigate the intrinsic kinetics of hydrogenation of butynediol to cis-2-butenediol, using a modified Pd-Zn-$CaCO_3$ catalyst. This being a multiphase system, it was important to insure that mass transfer and hydrodynamic factors were either eliminated or accounted for in determining the kinetics. For this purpose, a fine size of catalyst particles was used ($d_p = 4 \times 10^{-2}$ m) so as to eliminate intraparticle and liquid-particle mass transfer resistances. Also, the data were obtained under stirring speeds well beyond the critical speed of agitation required for complete suspension of particles. The critical speed calculated by the correlation of Zwietering (1958) was 3.5 Hz for the highest catalyst loading of 1.1 kg/m^3 used in this work. In order to evaluate the importance of various mass transfer resistances, the criteria suggested by Ramachandran and Chaudhari (1983) were used.

From the preliminary experiments, it was observed that the catalyst system Pd-Zn-$CaCO_3$ was highly selective for hydrogenation of butynediol to cis-butenediol and only this single reaction occurred in the range of conditions studied. The material balance of butynediol converted, H_2 consumed, and butenediol formed were consistent with the stoichiometric reaction given above to the extent of 95–98% in all the experiments. Therefore, for most of the kinetic runs the change of H_2 pressure with time was observed under different operating conditions. It was also

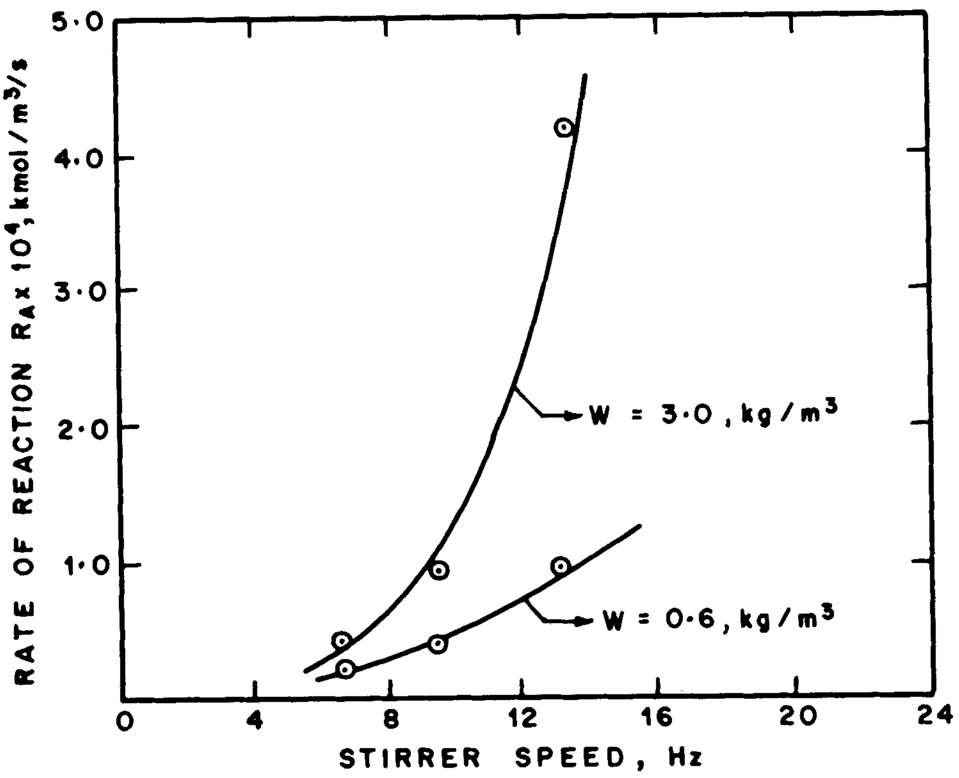

Figure 5. Effect of stirrer speed on reaction rate at 343 K.

insured by catalyst recycle experiments that the activity of the catalyst remained unchanged even after repeated use. From the pressure of H_2 vs. time data, initial rates of reaction were calculated. The initial rate data were obtained in the range of variables given earlier. The interpretation of the initial rate data and the batch reactor performance is discussed in the following sections.

Analysis of Initial Rate Data

The initial rates calculated from the pressure of H_2 vs. time data were found to be reproducible within 5–7%, as confirmed by repeated experiments under a few selected conditions. As the material balance agreed well as per the stated reaction, these data can be confidently used to develop a kinetic model. The initial rate data were used to first evaluate the significance of various mass transfer resistances. For this, the criteria suggested by Ramachandran and Chaudhari (1983) were used and the details of these are given in the Appendix. From this analysis, it was found that for the data at 303, 333, and 323 K the mass transfer resistances were negligible. However, the data at 343 K indicated significant gas-liquid mass transfer resistance. The dependence of the rates on various parameters is discussed below.

Figures 1–3, show the effects of catalyst loading, pressure of H_2, and butynediol concentration on the rate of hydrogenation, for 303–323 K. The rate varied linearly with catalyst concentration, which is consistent with the absence of gas-liquid mass transfer resistance. The dependence of rate on H_2 pressure is nonlinear and indicates fractional ($\simeq 0.5$) order-dependence with respect to H_2. The concentration of butynediol adversely affected the rate of hydrogenation beyond 5% concentration. This is a typical case of substrate inhibited kinetics and needs to be considered carefully in kinetic modeling. The effect of butenediol (product) concentration on the initial rates is shown in Figure 4 which clearly indicates that the rate of hydrogenation is not affected in the presence of product. In order to check the significance of gas-liquid mass transfer resistance, experiments were carried out at different agitation speeds at 313, 323, and 343 K. At 313 and 323 K, the rate was found to be unaffected by agitation speed, while at 343 K the rate is strongly dependent on agitation speed; see Figure 5. This agrees with the conclusion drawn from quantitative criteria that at 343 K, gas-liquid mass transfer resistance is significant, while at lower temperatures it is not important. It may also be noted that at higher catalyst loadings, the effect of agitation is more pronounced as compared to the lower catalyst loading, an observation consistent with gas-liquid mass transfer as controlling.

The rate data in the kinetic regime (303–323 K) were fitted to the rate equations, some purely empirical and some corresponding to Langmuir-Hinshelwood models. The list of equations considered along with the best parameters obtained are presented in Table 1. A nonlinear least-squares regression analysis was used with each equation in Table 1 to determine the best parameters for each model. The values of ϕ_{min}, the minimized sums of square of the difference between the observed and predicted rates are also listed in Table 1. It was found that only for Eq. 1 were the values of rate parameters positive for all the temperatures.

$$R_A = \frac{wk\sqrt{P_{gA}/H_A}B_1}{(1 + K_B B_1)^2} \tag{1}$$

Also, ϕ_{min}, was lowest for Eq. 1 at all temperatures. This suggests that Eq. 1 is the best model to represent the kinetics of butynediol hydrogenation over the entire range of conditions studied. The rates predicted using Eq. 1 were found to agree within 5–7% error with the experimental rates.

The half-order with respect to H_2 at all temperatures might be interpreted as the basis for suggesting that adsorption of H_2 occurs dissociatively. Thus, if we assume following reaction mechanism,

$$B + s \rightleftharpoons B_s$$

TABLE 1. RATE EQUATIONS USED FOR FITTING THE KINETIC DATA AND PARAMETERS OBTAINED

Model No.	Rate Equation	Temp. K	k**	K_A m^3/kmol	K_B m^3/kmol	ϕ_{min} kmol/m^3/s
1.	$\frac{wk\sqrt{P_{gA}/H_A}B_1}{(1+K_BB_1)^2}$	303	0.0116	—	0.267×10	0.758×10^{-10}
		313	0.0161	—	0.292×10	0.789×10^{-10}
		323	0.0263	—	0.322×10	0.142×10^{-8}
		343*	0.0664	—	0.421×10	—
2.	$\frac{wk(P_{gA}/H_A)B_1}{(1+K_A(P_{gA}/H_A))(1+K_BB_1)^2}$	303	0.596	0.065×10^3	-0.595×10^2	0.444×10^{-7}
		313	0.438	-0.556×10^2	-0.798×10^3	0.580×10^{-7}
		323	0.409	0.603×10^2	0.321×10	0.148×10^{-8}
3.	$\frac{wk(P_{gA}/H_A)B_1}{(1+(K_AP_{gA}/H_A)+K_BB_1)^2}$	303	0.590	0.652×10^3	-0.590×10^2	0.442×10^{-7}
		313	-0.430×10^2	-0.546×10^2	0.292×10	0.567×10^{-8}
		323	0.859	0.592×10^2	0.686×10	0.196×10^{-8}
4.	$\frac{wk(P_{gA}/H_A)B_1}{(1+(K_AP_{gA}/H_A)+K_BB_1)}$	303	0.241×10^{-2}	-0.125×10^3	0.164×10	0.483×10^{-7}
		313	0.661×10^{-1}	-0.155×10^4	0.534	0.907×10^{-7}
		323	0.322×10^{-3}	-0.124×10^{18}	0.230×10^{16}	0.315×10^{-6}
5.	$\frac{wk(P_{gA}/H_A)B_1}{(1+K\sqrt{P_{gA}/H_A}+K_BB_1)^2}$	303	0.442×10	-0.151×10	0.181×10^2	0.213×10^{-8}
		313	0.205×10^{10}	0.115×10^7	-0.322×10^8	0.118×10^{-6}
		323	0.745	0.388×10^2	-0.662×10^2	0.289×10^{-6}
6.	$\frac{wk(P_{gA}/H_A)B_1}{(1+K\sqrt{P_{gA}/H_A}+K_BB_1)^3}$	303	0.970×10^{-1}	0.296×10^{-1}	0.124×10	0.616×10^{-9}
		313	0.109×10	0.311	0.278×10	0.155×10^{-8}
		323	0.118	-0.720×10^{-2}	0.116×10	0.448×10^{-8}

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* The parameters at 343 K were evaluated by incorporating mass transfer effects as discussed in the text.

** Units of k are (m^3/kg/s)(m^3/kmol)$^{1/2}$ in model 1, and (m^3/kg/s)(m^3/kmol) in models 2–6.

$$H_2 + 2s \rightleftharpoons 2Hs$$

$$B_s + H_s \rightleftharpoons BH_s + s$$

$$BH_s + H_s \rightleftharpoons P_s$$

$$P_s \rightleftharpoons P + s$$

and that the $B_s + H_s$ step is rate controlling, the following rate equation can be derived:

$$R_A = \frac{wk\sqrt{P_{gA}/H_A}B_1}{(1 + \sqrt{K_A(P_{gA}/H_A)} + K_BB_1 + K_PP_1)^2}$$

For $(K_AP_{gA}/H_A)^{1/2}$ and K_pP_1 very much lower than 1, the above equation reduces to Eq. 1. Thus the above reaction mechanism appears likely for hydrogenation of butynediol.

Batch Reactor Models

Several experiments were carried out in which decrease in pressure vs. time data were observed under various operating conditions. In a batch slurry reactor, the pressure of H_2, concentration of liquid reactant (butynediol), and product (butenediol) vary simultaneously as a function of time and hence it was thought necessary to check the validity of the rate equation over the entire range of conditions involved in batch reactors operated at higher conversions. In this section, the models for a constant and variable pressure batch slurry reactor have been described and the predictions of the model compared with experimental results over a wide range of conditions. The system under consideration involves a pure gas phase reactant A (hydrogen), an aqueous liquid phase reactant B (butynediol), and the suspended solid catalyst. For the kinetic regime, and assuming Eq. 1 is applicable, the relevant mass balance equations are:

$$-\frac{dP_{qA}}{dt} = \left[\frac{RTV_Lw}{V_g}\right]\left[\frac{k\sqrt{P_{gA}/H_A}B_1}{(1+K_BB_1)^2}\right] \tag{2}$$

$$-\frac{dB_1}{dt} = \frac{\nu_Bwk\sqrt{P_{gA}/H_A}B_1}{(1+K_BB_1)^2} \tag{3}$$

and

$$\frac{dE_1}{dt} = \frac{\nu_Ewk\sqrt{P_{gA}/H_A}B_1}{(1+K_BB_1)^2} \tag{4}$$

with the initial conditions that at $t = 0$, $P_{gA} = P_{gAi}$, $B_1 = B_{1i}$ and $E_1 = 0$.

From Eqs. 2 and 3, we obtain the following relationship between the concentration of butynediol, B_1, and the pressure of H_2, P_{gA} at any time in the batch reactor

$$B_1 = B_{1i} - \frac{1}{\alpha}(P_{gAi} - P_{gA}) \tag{5}$$

Substituting Eq. 5 in Eq. 2, B_1 can be eliminated in terms of P_{gA} to obtain the following expression in terms of only P_{gA}:

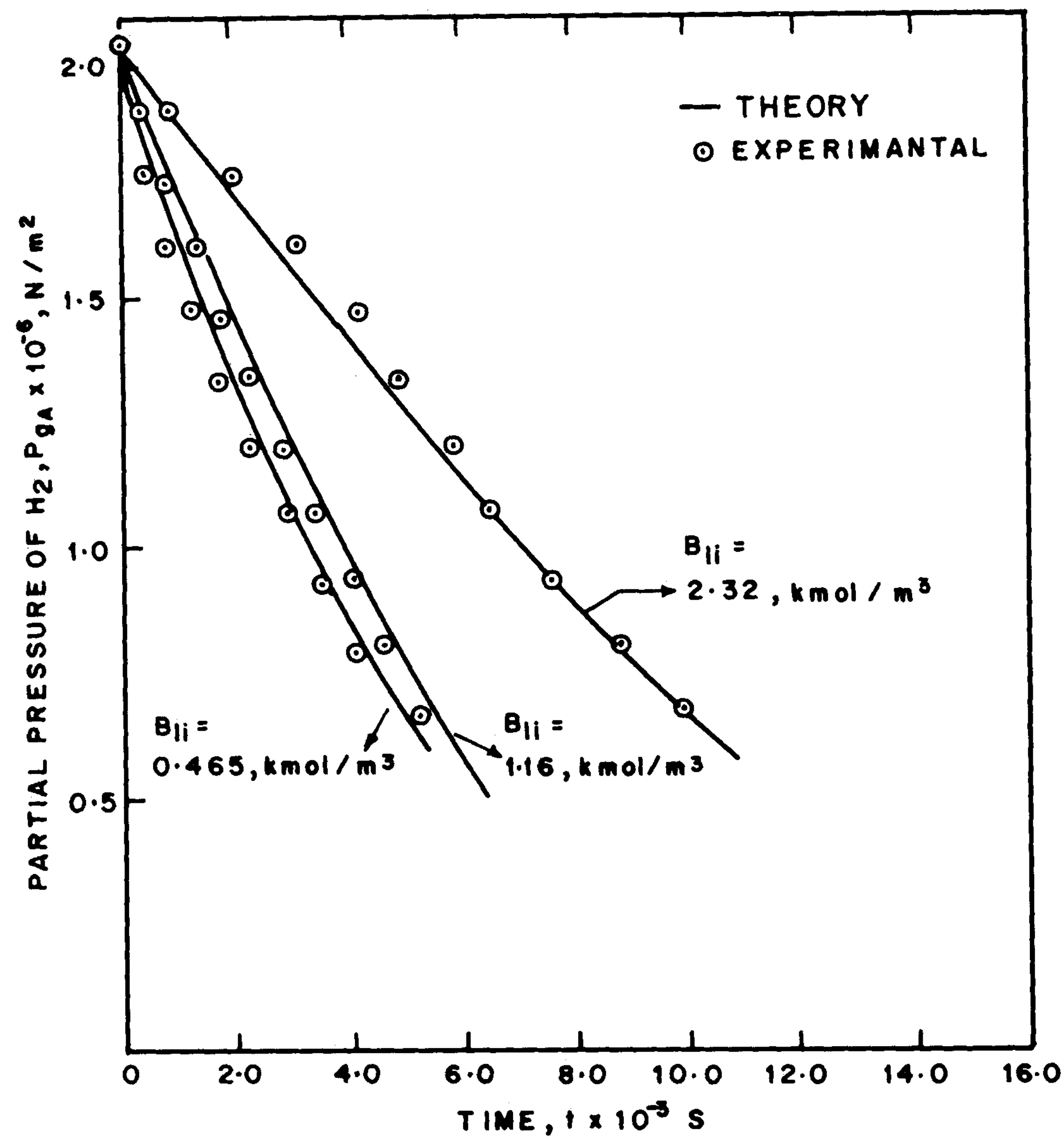

Figure 6. P_{gA} vs. t data for various butynediol concentrations at 303 K.
Catalyst loading, w, 1.10 kg/m^3; Stirrer speed, 15 Hz

$$-\frac{dP_{gA}}{dt} = \frac{RTV_L wk\sqrt{P_{gA}H_A}\left[B_{1i} - \frac{1}{\alpha}(P_{gAi} - P_{gA})\right]}{V_g\left[1 + K_B\left\{B_{1i} - \frac{1}{\alpha}(P_{gAi} - P_{gA})\right\}\right]^2} \qquad (6)$$

In order to predict a decrease in pressure vs. time, we have to integrate only Eq. 6, and then B_1 at any time can be predicted using Eq. 5. In Eq. 6, the influence of changing concentration of the reactant, B_1, as well as pressure is taken into account and can be solved numerically using the Runge-Kutta method.

In the presence of gas-liquid mass transfer, the following expression for the overall rate of reaction can be derived.

$$R_A = \frac{[(\beta^2/k_La_B)^2 + 4\beta^2P_{gA}/H_A]^{0.5} - (\beta^2/k_La_B)}{2} \qquad (7)$$

The relevant equation for the batch reactor is:

$$-\frac{dP_{gA}}{dt} = \frac{RTV_L}{V_g}\left[\frac{[(\beta^2/k_La_B)^2 + 4\beta^2P_{gA}/H_A]^{0.5} - (\beta^2/k_La_B)}{2}\right] \qquad (8)$$

With appropriate substituting for B_1 in terms of P_{gA} from Eq. 5, we obtain Eq. 8 in terms of P_{gA} as a variable with an additional parameter k_La_B. For a given set of parameters (k, K_B, and k_La_B), Eq. 8 can be integrated numerically to obtain P_{gA} vs. time predictions.

For constant pressure conditions, an analytical solution for the concentration profile of B_1 can be obtained by solution of Eq. 3. For the kinetic regime, the solution is:

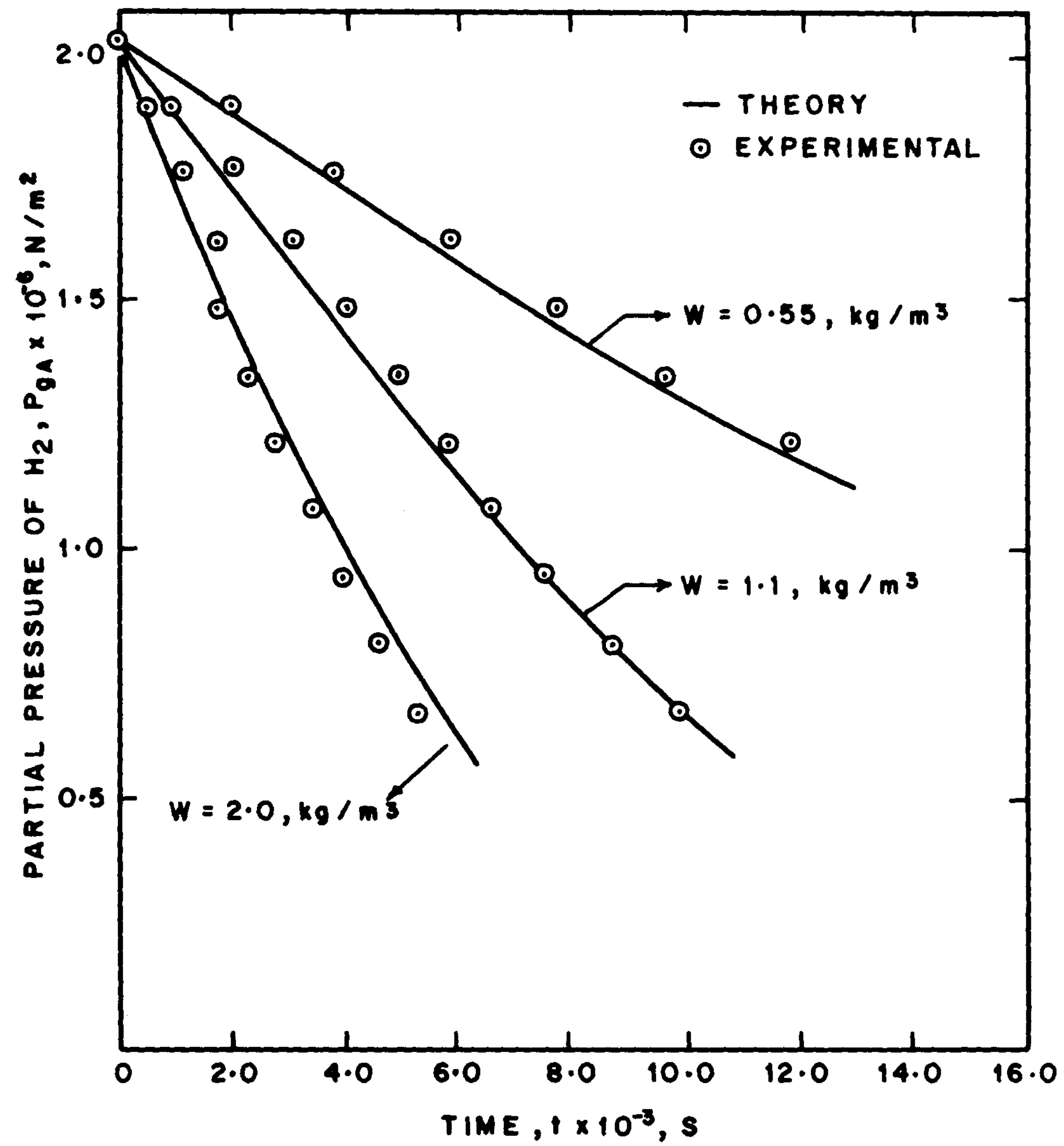

Figure 7. P_{gA} vs. t data for various catalyst concentrations at 303 K.
Initial butynediol concentration, B_{1i}, 2.32 kmol/m³; stirrer speed, 15 Hz

$$\ln(B_{1i}|B_1) + 2K_B(B_{1i} - B_1) + \frac{1}{2}K_B^2(B_{1i}^2 - B_1^2) = \nu_B w k t\sqrt{P_{gA}/H_A} \quad (9)$$

The charts of concentration vs. time can be predicted using Eq. 9. Then from the stoichiometric relationship, the product concentration profile can also be predicted. The above set of equations can also be used to evaluate kinetic parameters by simulating the observed concentration profiles and the model predictions.

Comparison of Experimental and Predicted Results

In order to verify the applicability of the kinetic model over a wide range of conditions, batch reactor data under variable and constant pressure conditions were obtained at different conditions. The predictions of the batch reactor model were compared with these results.

Pressure of H_2 vs. Time Data. For 303 K, decrease in pressure vs. time data were observed at different initial pressures, concentrations of butynediol, and catalyst loadings. Some of the results are shown in Figures 6 and 7. For these conditions, the results were also predicted by numerical integration of Eq. 6, using values of k and K_B as 0.0116 (m³/kg/s) (m³/kmol)$^{0.5}$ and 2.67 m³/kmol, respectively. These are also shown in Figures 6 and 7. It can be noted that the predictions of the model agree with experiments within a maximum error of about 6%, thus indicating the validity of the rate equation over a wide range of concentrations of the reactant. The decrease in the rate with increase in butynediol concentration can also be seen from the data shown in Figure 6. In order to confirm that the rate model is applicable at higher temperatures, the comparison of the experimental pressure vs. time data with those predicted by numerical integration of Eq. 6 was made for 313 and 323 K. Here at each temperature, the values of k and K_B evaluated from initial rate data (Table 1) were used. Here

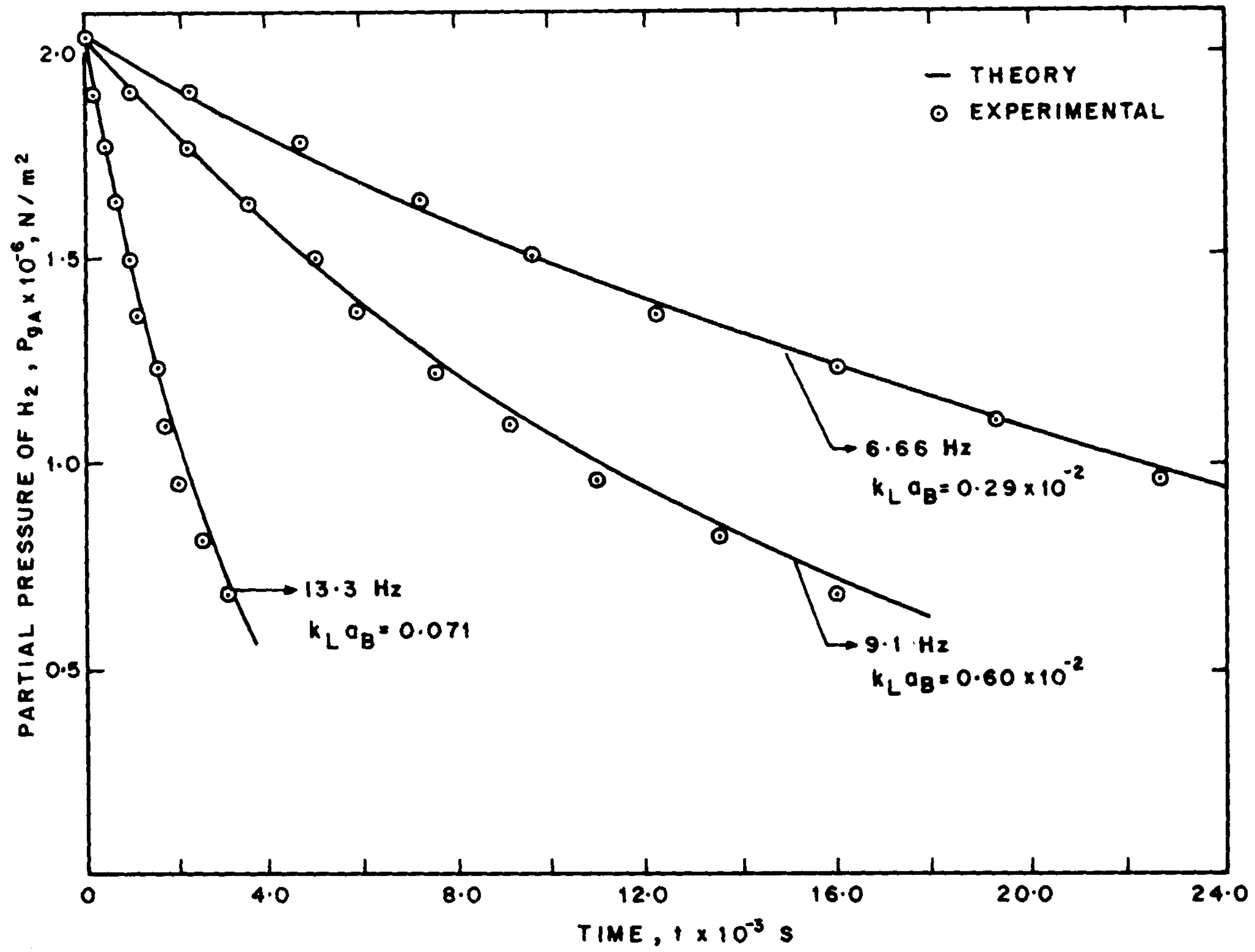

Figure 8. Effect of stirrer speed on hydrogenation rate at 343 K.
Catalyst loading, w, 3.0 kg/m³, butynediol concentration, B_{li}, 2.32 kmol/m³

too, the agreement between experiments and predicted results was found to be within 5–7%, error thus further confirming the applicability of the kinetic model.

For the data at 343 K, it was found from the preliminary analysis that gas-liquid mass transfer was important. The H_2 pressure vs. time data for 343 K at different agitation speeds, are shown in Figure 8. The strong influence of agitation speed is also consistent with our conclusion of gas-liquid mass transfer being significant. The data obtained at 343 K were used to evaluate the kinetic parameters k, K_B, and the mass transfer coefficient $k_L a_B$ by fitting the experimental data with the numerical solution of Eq. 8. For this purpose the initial trial values of k and K_B wer chosen from extrapolation of the data obtained at 303–323 K. The predictions of the numerical solution are also shown in Figure 8 for the best values of the parameters. It can be noted that for $k = 6.64 \times 10^{-2}$ $(m^3/kg/s)(m^3/kmol)^{0.5}$ and $K_B = 4.2$ m³/kmol, the experimental data agree with predicted results at different conditions. For different stirrer speeds, $k_L a_B$ values were also evaluated. On comparison of these values with the predictions of literature correlations (such as Bern et al., 1976, and Yagi and and Yoshida, 1975), it is observed that the values obtained in this work are lower. This can be explained on the different hydrodynamic conditions encountered in the reactor used. The literature correlations are based on a system wherein gas is continuously bubbled through slurry phase and are in terms of a linear gas velocity. In the present work a batch pressure autoclave was used in which gas is not sparged but is sucked in merely by the agitation system, hence lower interfacial area is likely to exist.

Constant Pressure Data. Some experiments were carried out at constant H_2 pressure in which the liquid reactant and product concentration profiles were observed. The results at 313 and 323 K are shown in Figure 9. For this case the liquid phase reactant concentration vs. time can be predicted using Eq. 9 for appropriate values of k and K_B. Also shown in Figure 9 are the predicted results using Eq. 9. It can be seen that the model predictions agree well with experiments within a maximum error of about 5–6%. As ultimately the quantity of interest is the liquid conversion, these experiments were carried out. An interesting observation in Figure 9 is that the nature of butynediol concentration vs. time curve is concave which is normally expected for a -ve order kinetics. This further supports that the kinetic model is applicable over a wide range of conditions.

Results on Two-Liter Scale. In order to check the scale-up effect, concentration profiles of butynediol and butenediol were observed in a two-liter autoclave at 313 K, catalyst loading of 1.2 kg/cm³, H_2 pressure of 2.067×10^6 N/m² and 15 Hz. Figure 10 shows the

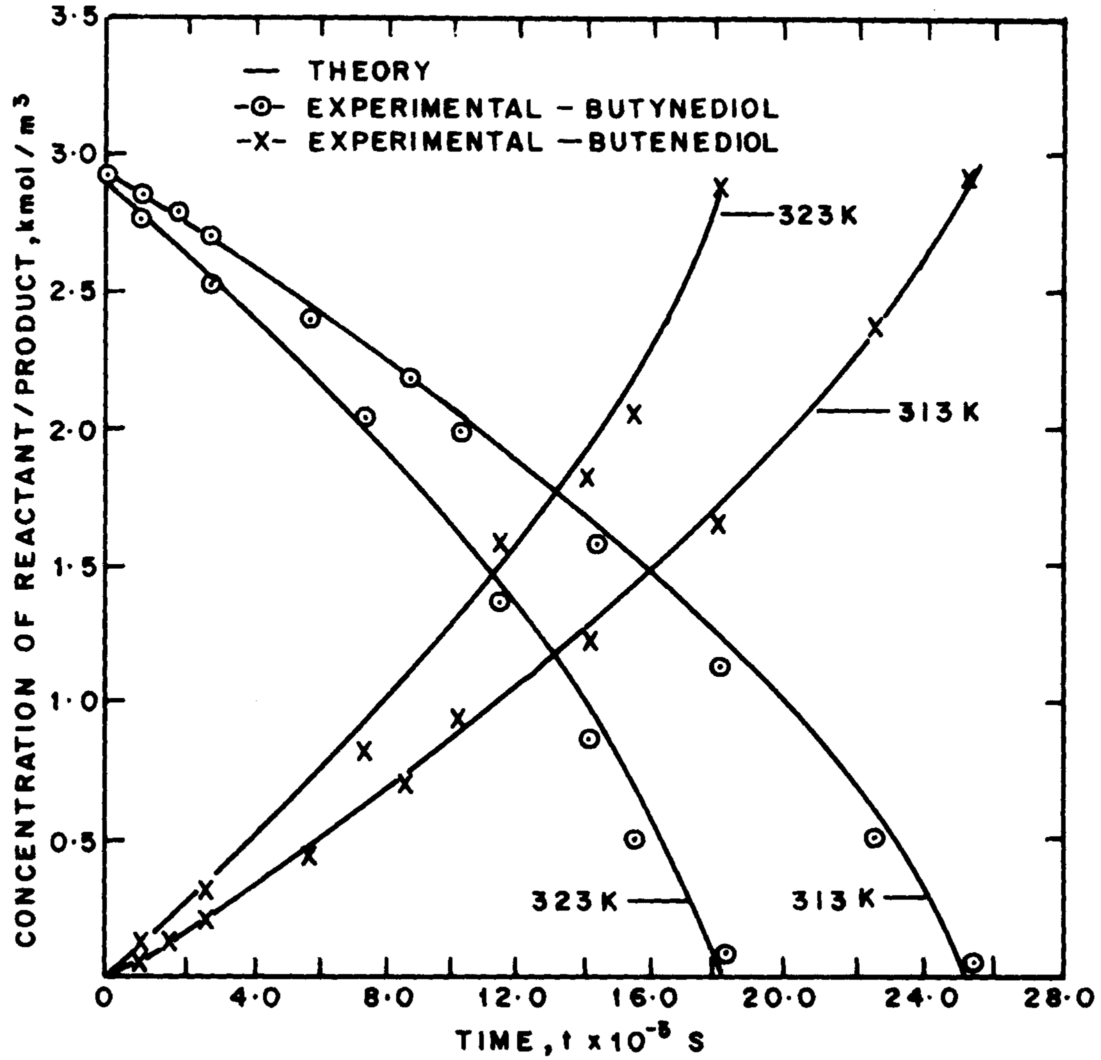

Figure 9. Liquid reactant/product concentration profile in a 0.6 L batch reactor.
Catalyst loading, w, 1.1 kg/m^3; partial pressure of H_2, P_{gA}, 2.067 × 10^6 N/m^2; stirrer speed, 15 Hz

experimental data along with the theoretical predictions using Eq. 9. The excellent agreement between the predicted and experimental data indicates that the rate equation can be confidently used for scale-up purposes.

Temperature-Dependence of Rate Parameters. The temperature-dependence of the reaction rate constant k and the adsorption equilibrium constant K_B is shown in Figure 11 as a semilog plot of k or K_B vs. $1/T$. From the slopes of these plots the activation energy of the reaction and heat of adsorption were found to be 38.30 J/kmol and −9.87 J/kmol, respectively. The negative value of the heat of adsorption $(-\Delta H)$ indicates a possibility of endothermic chemisorption. Such observation, though uncommon, has also been made earlier (Broderick and Gates 1981).

SUMMARY

Hydrogenation of butynediol to butenediol was studied using Pd-Zn-$CaCO_3$ catalyst in a high-pressure slurry reactor. The kinetics of the reaction was studied from initial rate data and the following rate equation is proposed:

$$R_a = \frac{wk\sqrt{P_{gA}H_A}B_1}{(1 + K_B B_1)^2}$$

It was found that at 303–323 K mass transfer effects were unimportant, while at 343 K gas-liquid mass transfer resistance was significant. The applicability of the kinetic model has been demonstrated by comparing the experimental and predicted integral batch reactor data. The pressure vs. time data can also be used to evaluate the kinetic parameters. From 343 K data, the values of k, K_B, and gas-liquid mass transfer coefficients $(k_L a_B)$ were evaluated using batch reactor models incorporating the effect of mass transfer. Finally, the applicability of the rate equation is demonstrated to predict the liquid concentration profile in a batch reactor and for scale-up purposes. The excellent agreement between the predicted and experimental results suggest that the rate equation can be confidently used for scale-up and design purposes.

NOTATION

a_B = effective gas-liquid interfacial area per unit volume of the reactor, m^2/m^3
A_1 = concentration of dissolved hydrogen in the bulk liquid, kmol/m^3

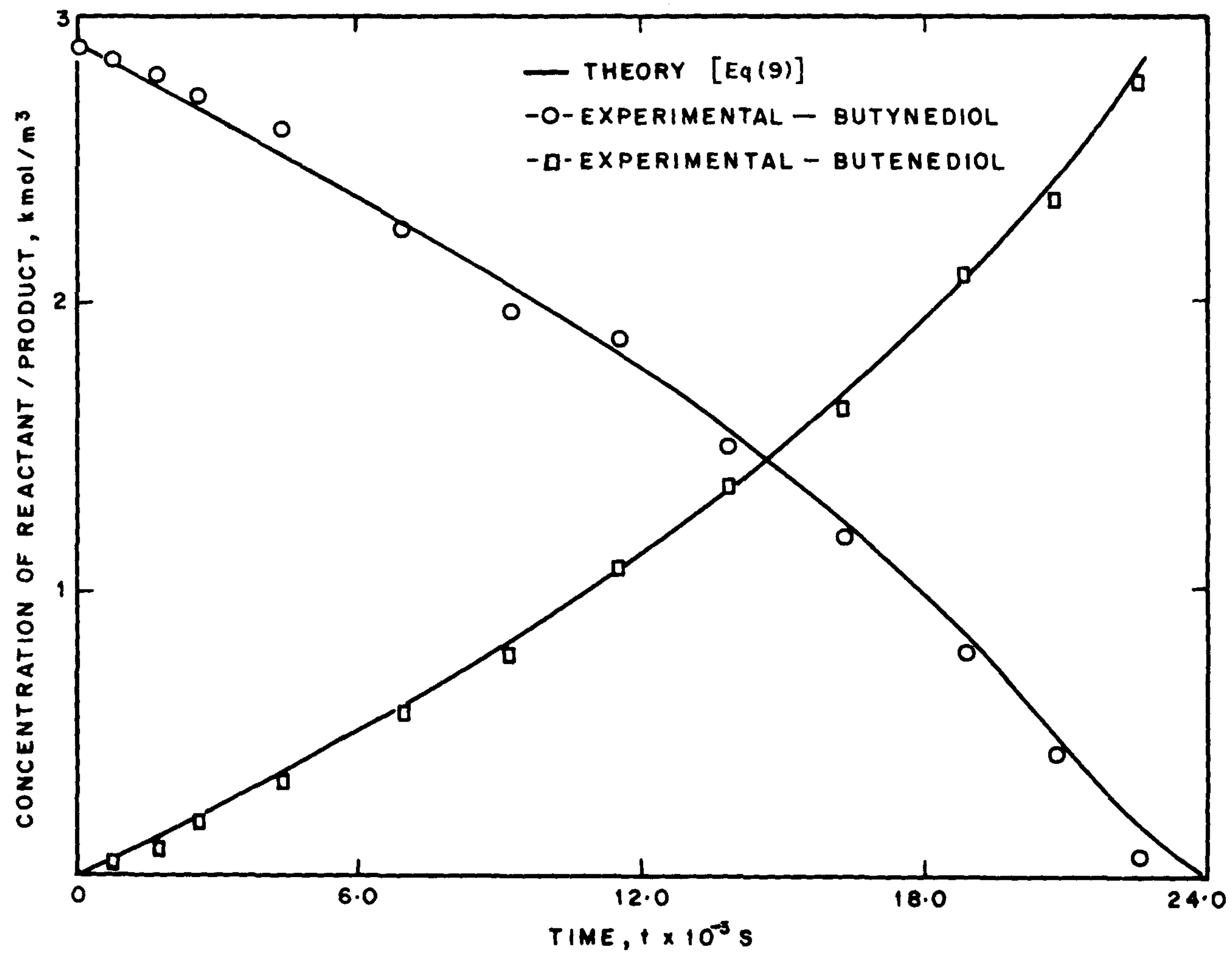

Figure 10. Liquid reactant/product concentration profile in a 2 L batch reactor at 313 K.
Catalyst loading, w, 1.2 kg/m³; partial pressure of H_2, P_{gA}, 2.067 × 10^6 N/m²; stirrer speed, 15 Hz

B_l = concentration of butynediol, kmol/m³
B_{li} = initial concentration of butynediol, kmol/m³
d_p = particle size of catalyst, m
d_I = impeller diameter, m
D = diffusivity of H_2 in liquid, m²/s
D_e = effective diffusivity of H_2 in liquid filled pores, m²/s
e = energy supplied to liquid
E_l = concentration of product (butenediol), kmol/m³
F_c = shape factor of catalyst particles
H_A = Henry's law constant for solubility of a, m³/mol/(N/m²)
k = reaction rate constant (m³/kg)(m³/kmol)$^{0.5}$/s
k_L = liquid-solid mass transfer coefficient, m/s
K_B = constant in rate Eq. 1, m³/kmol
N = agitation speed, Hz
P_{gA} = partial pressure of H_2, N/m²
P_{gAi} = partial pressure of hydrogen at $t = 0$, N/m²
R_A = overall rate of reaction, kmol/m³/s
R = gas constant, (N/m²)m³/kmol/K
t = time elapsed since the start of reaction, s
T = temperature, K
V_g = volume of gas phase in the reactor, m³
V_L = volume of liquid phase in reactor, m³
w = mass of catalyst per unit volume of slurry, kg/m³

Greek Letters

α = parameter defined as $RTV_L/\nu_B V_g$
α_1 = parameter defined by Eq. 10
α_2 = parameter defined by Eq. 11
β = parameter defined as $wkB_l/(1 + K_B B_l)^2$
ν_B = stoichiometric coefficient for species E
ν_E = stoichiometric coefficient for species E
ϵ = porosity of catalyst particles
$-\Delta H$ = heat of adsorption, J/kmol
ϕ_{exp} = experimental Thiele parameter defined by Eq. 12
ϕ_{min} = minimum of sum of squares of the differences in predicted and measured rates
ρ_L = liquid density, kg/m³
ρ_p = catalyst particle density, kg/m³
μ_L = viscosity of liquid, kg/m/s

APPENDIX

For ascertaining the contribution of various mass-transfer resistances, the following criteria described by Ramachandran and Chaudhari (1983) were used.

(a) Absence of gas-liquid mass transfer, if,

$$\alpha_1 = \frac{R_A H_A}{k_L a_B P_{gA}} < 0.1 \qquad \text{(A1)}$$

(b) Absence of liquid-solid mass transfer, if,

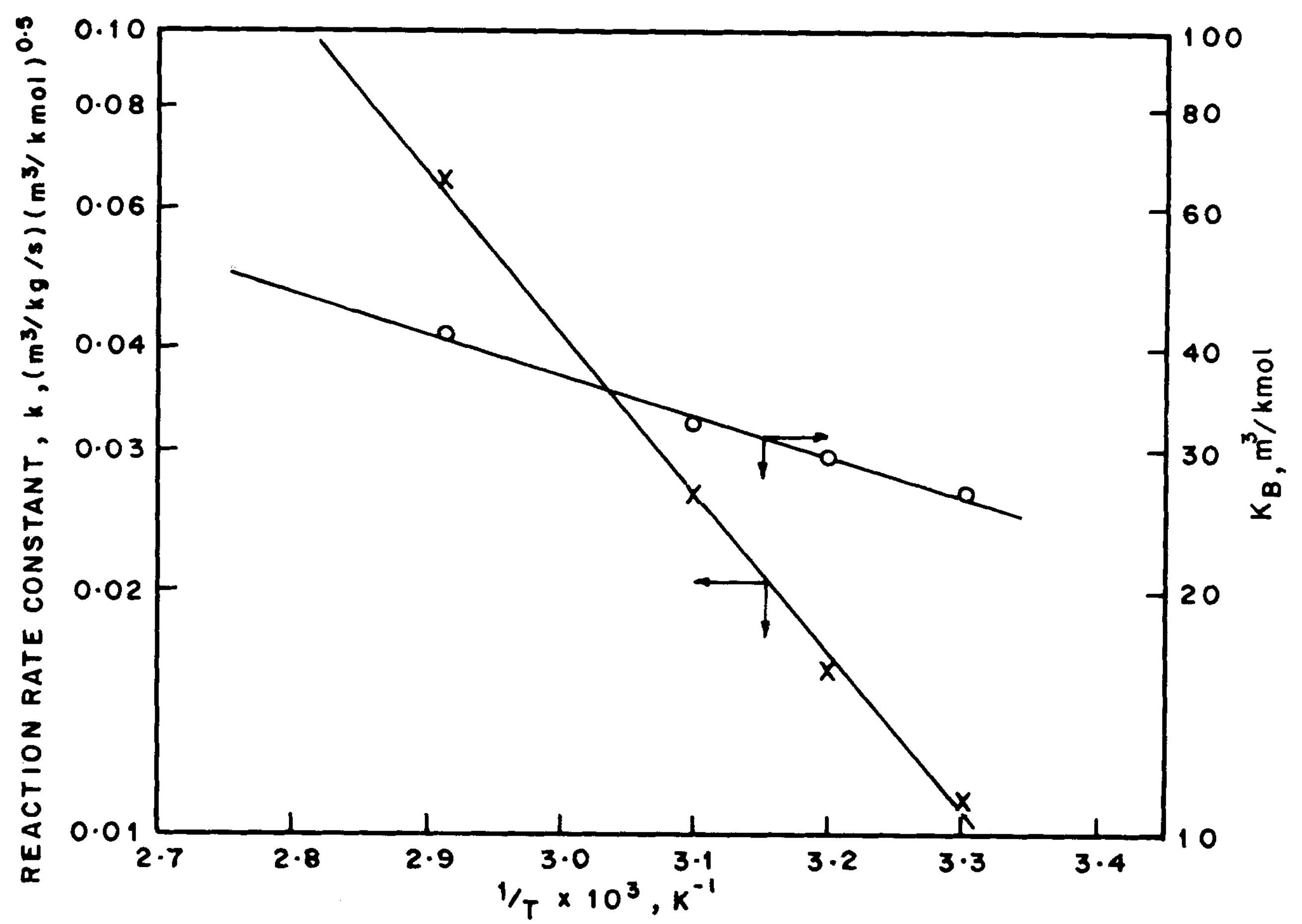

Figure 11. Temperature-dependence of the rate parameters.

$$\alpha_2 = \frac{R_A \rho_p d_p H_A}{6 k_s w P_{gA}} < 0.1 \qquad \text{(A2)}$$

(c) Absence of pore diffusion, if,

$$\phi_{\exp} = \frac{d_p}{6}\left[\frac{\rho_p R_A H_A}{w D_e P_{gA}}\right]^{0.5} < 0.2 \qquad \text{(A3)}$$

For the above calculations, solubility data were used from the work of Brahme et al. (1981), while the other parameters, D_e, $k_L a_B$, and k_s, were calculated from the following correlations:

$$D_e = D\epsilon/\tau \text{ (Satterfield, 1970)} \qquad \text{(A4)}$$

$$k_L a_B = 1.099 \times 10^{-2} N^{1.66} d_I^{1.98} u_g^{0.32} V_L^{-0.52}$$
$$\text{(Bern et al., 1981)} \qquad \text{(A5)}$$

$$\frac{k_s d_p}{D F_c} = 2 + 0.4\left[\frac{e d_p^4 \rho_L^3}{u_L^3}\right]^{0.25}\left[\frac{\mu_L}{\rho_L D}\right]^{0.333}$$
$$\text{(Sano et al., 1974)} \qquad \text{(A6)}$$

For the above calculations, the molecular diffusivity D was calculated from the Wilke-Change (1955) equation; the tortuosity factor τ was assumed to be 3 (Satterfield, 1970); F_c, the shape factor, was taken as unity as spherical particles were used; and e, the energy supplied to the liquid, was calculated by the procedure described by Ramachandran and Chaudhari (1983).

It was observed that for the data of 303–323 K, the above criteria were satisfied, indicating absence of mass transfer effects. The data at 343 K showed α_1 values in a range of 0.5 to 1.0, showing significant gas-liquid mass transfer resistance.

LITERATURE CITED

Appleyard, C. J. S., and J. F. C. Gartshore, "Manufacture of Butynediol at IG," *Ludwigshafen BIOS Report 22*, 367 (1946).

Bern, L., J. O. Lidefelt, and N. H. Schoon, "Mass Transfer and Scale-Up in Fat Hydrogenation," *J. Am. Oil Chem. Soc.*, **53**, 463 (1976).

Broderick, D. H., and B. C. Gates, "Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalyzed by Sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$: The Reaction Kinetics," *AIChE J.*, **27**, 663 (1981).

Brahme, P. H., et al., "Solubility of Hydrogen in Aqueous Solution of 2-Butyne-1, 4-diol and 2-Butene-1,4-diol *J. Chem. Eng. Data*, **26**, 416 (1981).

Fukuda, T., and K. Tokishige, "Partial Hydrogenation of 1,4-Butynediol," *Bull. Chem. Soc. Japan*, **31**, 339 (1958).

Hoffman, H., et al., (BASF) "Catalysis for Hydrogenation of Butynediol to Butenediol," Germ. Offen., 2,431,929 (1976).

Lindlar, H. O., and R. Dubuis, "Palladium Catalyst for Partial Reduction of Acetylenes," *Org. Syn.*, **46**, 89 (1966).

Ramachandran, P. A., and R. V. Chaudhari, *Three-Phase Catalytic Reactors*, Gordon and Breach, New York (1983).

Sano, Y., et al., "Mass Transfer Coefficients for Suspended Particles in Agitated Vessels and Bubble Columns," *J. Chem. Eng. Japan*, **7**, 255 (1974).

Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," MIT Press, Cambridge, (1970).

Wilke, C. R., and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AICHE J.*, **1**, 264 (1955).

Wood, A. S., and J. M. Reitz, "Hydrogenation of Butynediol to Butenediol," Germ. Offen., 2,619,660; U.S. Appl., 574,572 (1976a).

———, "Hydrogenation of Butynediol to Butenediol," Ger. Offen., 2,605,241; U.S. Appl., 5,745,71 (1976b).

Yagi, H., and F. Yoshida, "Gas Absorption by Newtonian and Non-newtonian Fluids in Sparged Agitated Vessels," *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 488 (1975).

Zweitering, T. N., "Suspending of Solid Particles in Liquid by Agitators," *Chem. Eng. Sci.*, **8**, 244 (1958).

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